Axially Symmetric U-O-Ln and U-O-U containing molecules from the control of uranyl reduction with simple f-block halides

Axially Symmetric U-O-Ln and U-O-U containing molecules from the control of uranyl reduction with simple f-block halides

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Abstract: The reduction of U^{VI} uranyl halides or amides by simple Ln^{II} or U^{III} salts forms highly symmetrical, linear, oxo-bridged trinuclear U^{V}-Ln^{III}-U^{V}, Ln^{III}-U^{IV}-Ln^{III} and U^{IV}-U^{IV}-U^{IV} complexes or linear Ln^{III}-U^{V} polymers according to the stoichiometry and solvent choice. Reactions can be tuned to give one- or two-electron uranyl reduction. Some features of their reactivity and magnetism are discussed in the context of using a series of strongly oxo-coupled homo and heterometallic poly(f-block) chains to better understand fundamental electronic structure in the f-block.

The d^0f^0 uranyl ion, $[UO_2]^{2+}$, is the most common form exhibited by uranium in molecular complexes; it is a water-soluble ion with linear, strongly bonded and unreactive oxo groups.[1] The reduction to $[U^{V}O_2]^{+}$ and then insoluble U^{IV} by metals, minerals or microbes is important for keeping it immobilized in the environment and out of groundwater, but the mechanisms for this are still not clear.[2] The U^{V} uranyl ion can also provide better models for the highly radioactive and more oxo-basic f^1 neptunyl and plutonyl ions found in nuclear waste.[3]

Two seminal, co-incident reports of the potassium-reduced coordination polymer $\{[UO_2(py)_5][KI_2(py)_2]\}_\infty$ **A** showed that anaerobic U^{V} uranyl is stable against disproportionation;[4] since then significant advances have been made in isolating uranyl(V) complexes. The reductive oxo-functionalisation with Group 1,[5] Group 2,[1c] d-block, [1c, 6] rare earth,[6b, 7] actinides,[3a] and main group metals,[5c, 8,9] as well as silicon[1d, 5b, 10] is also possible. The linearity of the f^1-uranyl provides a rare opportunity in f-block chemistry to control the orientation of the magnetic vector, and uranyl(V)–transition metal single molecule magnets have been made through this oxo-bridging strategy.[3a,6a,7,11]. Lanthanide/actinide complexes are promising candidates for single molecular magnetism,[11a] and it has been proposed that an even higher degree of axial symmetry should produce exceptional molecular magnets.[12]

However, access to this new chemistry has almost exclusively been achieved through deployment of complicated polydentate ligands to saturate the equatorial coordination sphere of the uranyl ion.[13] The only examples of oxo-functionalisation of simple systems are from treatment of uranyl dichloride by a Group 1 reagent: these are the reduction by potassium to make **A**[4b] and reduction by $NaCH_2SiMe_3$ (followed by quenching with Me_3SiCl) to make $[U^{IV}(OSiMe_3)_2I_2(OPPh_3)_2]$ **B**.[14]

Here, we report how simple low oxidation state lanthanide and actinide salts can be used to oxo-coordinate and reduce simple uranyl(VI) salts to make new classes of stable, highly-symmetrical 4f- and 5f-ion oxo-bridged uranyl(V) and uranium(IV) complexes.

The U^{VI} uranyl complex $[UO_2Cl_2(THF)_2]$ reacts with 1.25 equiv. of a strongly reducing Ln^{II} halide; exemplified here by $[SmI_2(THF)_2]$ or DyI_2, in pyridine to form the reduced uranyl, U^{V}-Ln^{III}-U^{V} complexes $[\{UO_2(py)_5\}_2(LnI_4)]I$ (Ln = Sm (**1-Sm**, 40 %), Dy (**1-Dy**, 67 %), Scheme 1). The two (unisolated) by-products are $LnCl_3$ from the redox reaction and 0.25 equivalents of $LnCl_2$ which come from a halide exchange that ensures the products contain only iodide anions. Reactions carried out with 1 equiv of LnI_2 and additional iodide as $^{n}Bu_4NI$ also make **1** but less cleanly (see SI). The formal oxidation states are confirmed by elemental analysis, FTIR spectroscopy and single crystal X-ray diffraction (Figure 1 for **1-Sm** and SI for **1-Dy**). In agreement with the assigned formal oxidation states, an asymmetric [OUO] stretching frequency is located at 818 (**1-Sm**) and 825 cm^{-1} (**1-Dy**) (nujol). This indicates stronger U=O overlap in these mono-metallated $[O=U^{V}=O]^{+}$ units than in dipotassiated $[O=U^{V}=O]^{+}$ in **A** (ν_{OUO} = 797 cm^{-1}, KBr)[4a] although they are close to the dilithiated $[\{UO_2(py)_5\}\{Li_2(OTf)_3\}]_\infty$ (ν_{OUO} = 816 cm^{-1}, pyridine) and $[UO_2(OTf)(THF)_n]$ (ν_{OUO} = 812 cm^{-1}, pyridine) energies.[16]

When the U^{VI}/Sm^{II} reaction is repeated in acetonitrile the polymeric analogue $[\{UO_2I_4\}_2(Sm(NCMe)_6)]_n$ **2-Sm** (Ln = Sm) is isolated, Scheme 1b. Elemental analysis repeatedly gives a formula of $[\{UO_2I_4\}_2(Sm(NCMe)_5)]$, even for samples dried at ambient pressure. The solid-state structure (Fig. 1b) shows that the iodide ligands now bind equatorially to the uranyl, and the solvent molecules to the harder Sm cation, in contrast to **1**, but in accordance with the HSAB principle.

Once formed, polymeric **2-Sm** is no longer soluble, but FTIR spectra of the solid show that now both oxo groups of the uranyl are Ln-coordinated, the uranyl stretch is significantly weakened to 722 cm^{-1}. Unfortunately, the stronger reductant DyI_2 reacts with MeCN,[17] so we were unable to target **2-Dy**.

Reactions between $UO_2X_2(THF)_2$ and *two* equivalents of strongly reducing Dy^{II} or U^{III} form the linear, M-O-U^{IV}-O-M oxo-bridged trimers such as $[(UO_2I_4)\{UICl(py)_4\}_2]$ **4** (Scheme 1d, M = U^{IV}, X = Cl). Additionally, simple uranyl compounds other than the dichloride can be used; e.g. $[UO_2\{N(SiMe_3)_2\}_2(THF)_2]$ reacts with two Dy^{II} to form the linear, symmetrical Dy^{III}-U^{IV}-Dy^{III} complex $[(UO_2I_4)\{DyI(py)_5\}_2]$ **3-Dy** (see Figs. S14-16 for IR and Raman spectra).

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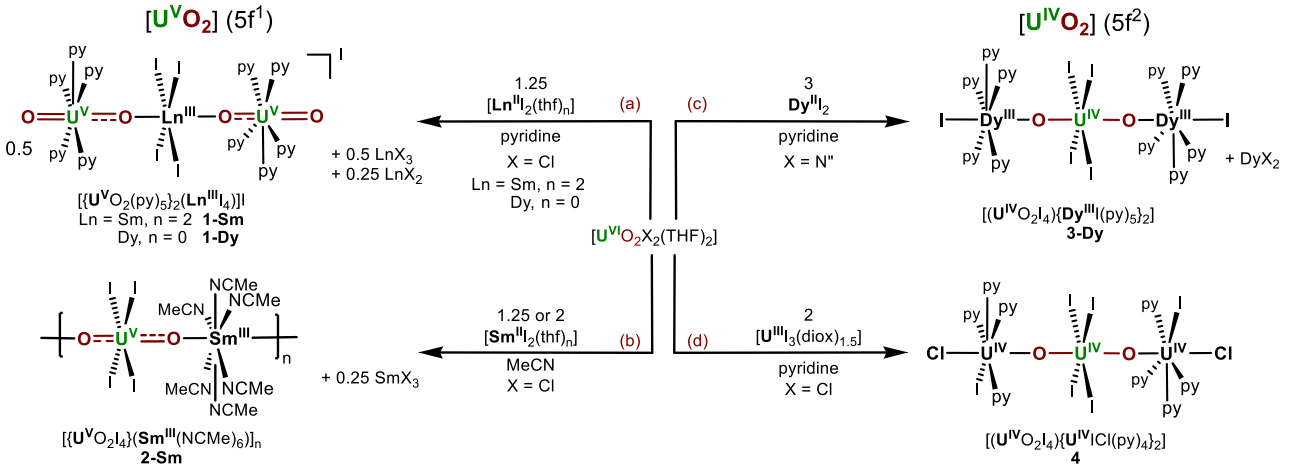
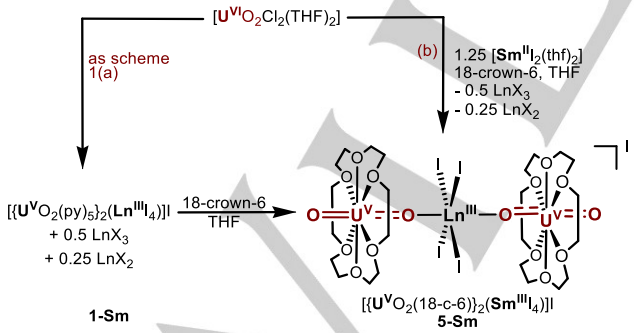


Scheme 1. Synthesis of mixed lanthanide-actinide complexes from 1-electron reduction (left hand side), and from 2-electron reduction (right hand side) of simple uranyl salts to afford the singly reduced uranyl complexes (a) $[\{UO_2(py)_5\}_2(LnI_4)]I$,**1-Sm** and **1-Dy** and (b) $[(UO_2I_4)(Sm(NCMe)_6)]_n$ **2-Sm**; and the doubly reduced uranyl salts (c) $[(UO_2I_4)\{DyI(py)_5\}_2]$ **3-Dy** and (d) $[(UO_2I_4)\{UICl(py)_4\}_2]$ **4**. N" = $N(SiMe_3)_2$; diox = dioxane.

When dissolved in pyridine both canary yellow **1-Sm** and cherry-red **1-Dy** give cherry red solutions. The UV/vis/NIR spectra exhibit strong, broadened absorptions with maxima at 461 nm (**1-Sm** ε = 2140 M^{-1} cm^{-1}) and 454 nm (**1-Dy** ε = 1249 M^{-1} cm^{-1}) and are assigned as π–π* processes. Additional *f-f* transitions were also observed between 650–1500 nm for complexes **1-Sm** (ε = 7–32 M^{-1} cm^{-1}) and **1-Dy** (ε = 13–34 M^{-1} cm^{-1}). Unfortunately, once precipitated from solution, **2-Sm, 4**, and **5-Sm** (see below) have very low solubility in organic solvents, frustrating NMR or quantitative UV/Vis/NIR spectroscopic investigation (see SI for solid state spectra).

Preliminary studies show that the equatorial ligands can be exchanged. For example, the addition of 18-crown-6 to the reaction between $[UO_2Cl_2(THF)_2]$ and $[SmI_2(THF)_2]$ in THF affords the crown-ether solvated U^V-Ln^{III}-U^V complex $[\{UO_2(18\text{-cr-}6)\}_2(SmI_4)]I$ **5-Sm** (Scheme 2; see SI for characterising data). Alternatively, the pyridine ligands of **1-Sm** can be substituted by 18-cr-6, underlining the stability of the U-O-Ln-O-U core.



Scheme 2. Reactions to afford the singly reduced uranyl $[\{UO_2(18\text{-cr-}6)\}_2(LnI_4)]I$,**5-Sm** either from the incorporation of 18-cr-6 in the reaction to form **1-Sm**, or from the reaction of **1-Sm.**

Complexes **1** are isostructural, with a linear, *pseudo-*D_{2h} [OUO]–Ln–[OUO] geometry (Figure 1). The uranium centres possess pentagonal bipyramidal geometry, retaining a *trans* di-oxo coordination (O–U–O = 177.8(3), U–O–Ln(1) = 176.1(3) and O–Ln(1)–O = 180.00(2)° in **1-Sm**). In agreement with the formal U^V oxidation state, both terminal U–O and Ln-bridged U–O distances are elongated with respect to uranyl dichloride; 1.802(6) and 1.915(6) Å respectively in **1-Sm**. The Sm–O and Dy–O bond lengths in **1** are consistent with a single bond (2.331(6) Å in **1-Sm**), but longer than those in our previously reported $[U^VO_2]^+$ *endo*-oxo-Ln-metallated $[\{UO_2Ln(py)_2(L^{Et})\}_2]$ **C** (Sm–O = 2.234(2) Å) (L^{Et} = Pacman-shaped pyrrole macrocycle),[6d,7] and *exo*-oxo-M-metallated $[(X_nM\text{-}OUO)\}(THF)(H_2L)]$ (M = Li, K, Mg, Al, Zn, U, Np)[1c,3a,15,9] The average U–O bond length of 1.859 Å in **1-Sm** is longer than that of 1.838 Å in the coordination polymer $\{[UO_2(py)_5][KI_2(py)_2]\}_\infty$ **A**.[4]

The mean U^V=O bonds in **2-Sm** (Fig. 1b) are 1.876 Å and Sm-O are 2.335 Å, in accordance with the assigned U^VSm^{III} formal oxidation states. The OUO unit remains essentially linear (OUO = 179.3(2)°) but overall the metal oxo chain waves due to a distortion of the OSmO bond to 145.6° as six coordinated MeCN molecules cannot fit in a purely equatorial plane.

The X-ray structures of **3-Dy** and **4** confirm that the double reduction and oxo-coordination remove any 'uranyl ion' character, but form strong M-O-M' interactions. We propose that the preferential coordination of I rather than py to the central U^{IV} is further indication of the loss of uranyl character, since the use of the majority of the valence orbitals in forming U=O bonds is a characteristic actinyl ion bonding feature. The Cl binding *trans* to the oxo in **4** is ascribed to its stronger *inverse trans influence* (ITI) than iodide.[18]

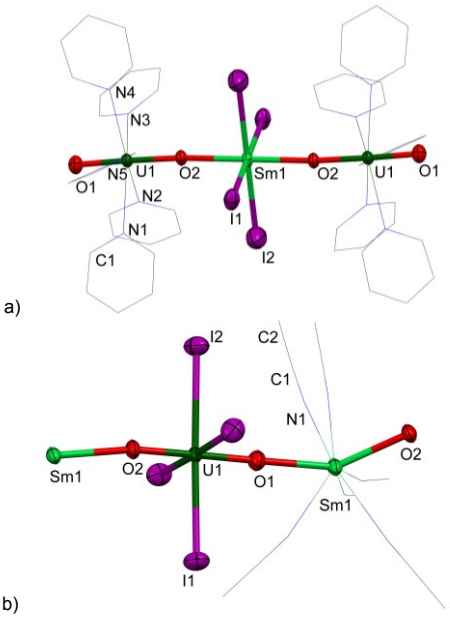


Figure 1. a) Solid-state structure of the cation of **1-Sm·3py** with ellipsoids drawn at 50% probability and coordinated solvent drawn wireframe. Hydrogen atoms, lattice solvent and iodide counter-anion are omitted for clarity. b) Solid-state structure of **2-Sm** with ellipsoids drawn at 50% probability and coordinated solvent drawn wireframe. Hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): (a) means: U-O 1.1.859, Sm-O 2.331, Sm-I 3.053, OUO = 177.81(2) U–N(py) 2.575(7)–2.623(8), Sm–I 2.993(1)–3.1137(6); (b) means: U-O 1.875, U-I 3.11, Sm-O 2.334, Sm-N 2.537, OUO = 179.3(2), OSmO 145.6(2).

The structures of **3-Dy·4py** and **4·4py** have *pseudo-D*$_{2h}$ or *C*$_{2h}$ symmetry, formally comprising $[U^{IV}O_2I_4]^{2-}$ and two *pseudo*-pentagonal bipyramidal $[Dy^{III}I(py)_5]$ or $[U^{IV}ICl(py)_4]^+$ caps respectively, and with O–U–O = 177.7(1)° in **3-Dy** and O–U–O = 180.0° in **4**. The U–O bond lengths in **3-Dy** are significantly shorter than those found for the central $[UO_2I_4]^{2-}$ unit in **4** (2.058(3) and 2.068(3) Å *versus* 2.166(5) Å), whereas the U–I bond lengths in **3-Dy** are significantly longer than those in **4** (3.1425(4)–3.1618(4) Å *versus* 3.0436(8)–3.0572(8) Å). Furthermore, the Dy–O bonds in **3-Dy** (2.126(3) and 2.119(3) Å) are significantly shorter than those in **1-Dy** (2.270(5) Å), consistent with reduction of U^V to U^{IV} and a more symmetrical oxo-bridging in **3-Dy**. In **4** the outer U(1)–O(1) bonds are much shorter than the central U(2)–O(1) in **4**, 2.042(5) vs 2.166(5) Å, but both are shorter than the average U-O bond in the CSD (2.361 Å).

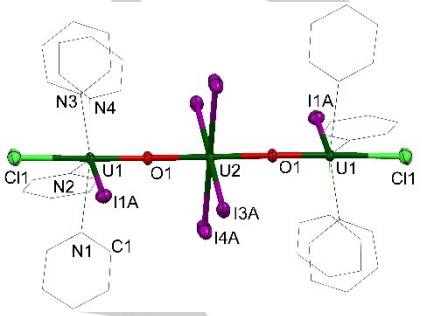


Figure 2. Solid-state structure of **4·4py** with ellipsoids drawn at 50% probability. H atoms, lattice solvent, and lower occupancy positions of the disordered I and N_3-py are omitted for clarity. Selected distances (Å) and angles (°): mean U-O 2.058(3), U2-I3 3.0571, U1-I1 3.0678(7), U-O-U 173.7, O-U-O 180.0.

Anticipating that the linear geometry of these complexes could generate interesting magnetic behavior, the dc magnetic susceptibility χ as a function of the temperature T for **1-Sm** and **4** were recorded (Figure **3**).

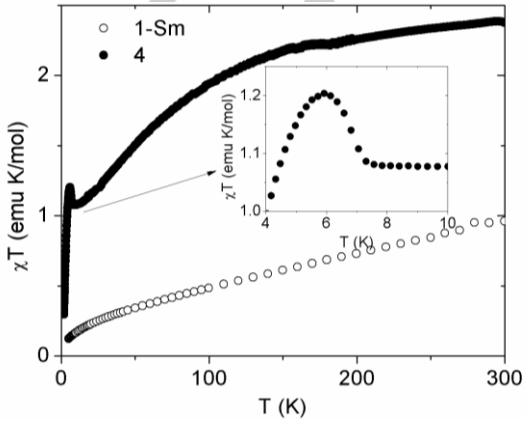


Figure 3: dc magnetic susceptibility χ as a function of temperature T (plotted as χT vs T) for **1-Sm** (open dots) and **4** (filled dots). The inset shows in detail the increase of χT with decreasing temperature between 8 and 6 K.

The susceptibility is significantly larger for **4** than for **1-Sm** over the whole investigated temperature range, a fact that is at first counterintuitive given that the latter complex is made up of three Kramers' ions whereas the former contains three non-Kramers ions. This is explained by considering that the free-ion effective magnetic moment μ_{eff} of U^{IV} is much larger than those of both U^V and Sm^{III}, and that the high-symmetry, linear geometry of **4** cannot completely remove the degeneracy of the low-energy ligand-field levels (and therefore cannot isolate a non-magnetic singlet as the ground state). Furthermore, whereas the susceptibility for **1-Sm** is essentially featureless, the χT vs T plot for **4** shows a clear upturn between 8 and 6 K followed by a sharp drop upon further decreasing the temperature. Such an upturn is usually considered as a signature of ferromagnetic coupling, but it is more likely that each of the two outer U^{IV} interacts antiferromagnetically with the central one, whilst also carrying a larger magnetic moment. Indeed, fitting the high-temperature part of the inverse susceptibility of **4** (Fig. S6) with a Curie-Weiss law $\chi^{-1} = 8(T - \Theta)/\mu_{eff}^2$ gives $\mu_{eff}^2 = 21.4\ \mu_B^2$ and a negative Curie-Weiss temperature Θ = -36.2 K, which indicates the presence of antiferromagnetic interactions. The effective magnetic moment is only slightly larger than that for two U^{IV} ions and much lower than for three. A similar situation was found in the trinuclear $Np^{VI/V}$ neptunyl complex $[(Np^{VI}O_2Cl_2)\{Np^VO_2Cl(THF)_3\}_2]$,[22] including the sharp downturn in χT at very low temperature which was attributed to magnetic saturation. Since this Np complex was also a single-molecule magnet with a high energy barrier to magnetic relaxation (about 100 cm^{-1}), we investigated the ac susceptibility of **4**, but did not

find any significant slowing down of the magnetic relaxation processes (Fig. S7).

An *a priori* prediction of which Ln or An salts would be capable of one or two electron uranyl reduction is complicated by the presence of strongly coordinating solvents, additional halides, a known propensity for these oxophilic metals to rapidly change coordination geometry, number, and their Lewis acidity. For example, the coordination of Lewis acidic Li^+, boranes, or 4f-cations to the U^{VI} uranyl oxo-group shifts the U^{VI} reduction by as much as +600 mV,[5a,10d] and uranyl iodides are easier to reduce than their chloride analogues; $UO_2I_2(py)_3$ can be reduced by the organic anions of the normally-stable organometallic $U(\eta\text{-}C_8H_8)_2$, to form a hexa-uranium cluster $U_6O_8I_8(py)_{10}$.[21]

In conclusion, we have demonstrated that redox reactions between readily accessible lanthanide and actinyl halides and related simple salts can produce linear oxo-coupled 4f/5f oligomers or infinite chains. These can be tuned for one or two-electron reduction, and mono- or di-oxo functionalisation. The reductants can be 4f (exemplified by Sm^{II} and Dy^{II}) or 5f cations (exemplified by U^{III}). Some post-synthetic modification has been demonstrated through simple L donor ligand exchange. The complexes are thermally stable, and most can be dissolved in a variety of aprotic solvents. Given their inherent symmetry and simplicity, these complexes may be an interesting and flexible system from which spectroscopic studies can elucidate more of the fundamental electronic structural details that are still missing for the f-block, in particular for the f^1 actinyl ions; preliminary magnetic analyses show strong antiferromagnetic coupling in the all-U system. Work is in progress to extrapolate these methods to the transuranic neptunyl and plutonyl cations, and to other combinations to explore the electronic structures of these systems.

Supporting information available

Full experimental and characterisation details, further IR, Raman, UV-Vis spectroscopic, and SQUID magnetometric data and analyses are included in the Supporting Information. CCDC 1549140-1549144, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: f-Element • Lanthanide • molecular magnetism • Reduction • Uranyl

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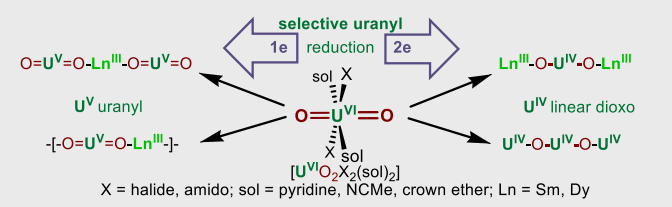
COMMUNICATION



Stuck on U: Simple, tuneable reactions between Ln(II) iodides and uranyl salts in pyridine or acetonitrile generate axially symmetric, one-or two-electron reduced, discrete or infinite, oxo-coupled 4f/5f systems, allowing fundamental electronic or magnetic properties to be tuned and studied.

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Axially Symmetric U-O-Ln and U-O-U containing molecules from the control of uranyl reduction with simple f-block halides